KINETICS OF INITIAL COAL HYDROGASIFICATION STAGES

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INTRODUCTION

For the last 15 years a strong incentive has existed in the United States to de-
velop the technology for commercial gasification of coals to yield high-methane-
content gas suitable as a substitute for natural gas. One of the general conclusions
derived from the many experimental studies conducted is that the yield of light
gaseous hydrocarbons, obtained during initial coal heat-up and for very short
periods thereafter, plays an important role in affecting the overall performances
and thermal efficiencies of any gasification process. It is during this initial gasi-
fication stage that coals undergo devolatilization reactions leading to the formation
of carbon oxides, water, oils and tars, and, most importantly, significant quantities
of light hydrocarbons — particularly methane — in the presence of hydrogen at
elevated pressures. Since, however, the exceptionally high reactivity most coals
exhibit for methane formation during initial reaction stages is transient, existing
only for a period of seconds at higher temperatures, rational design of commercial
systems to optimize methane yields requires as detailed a kinetic characterization
of pertinent processes occurring as is possible.

Because of its importance, this reaction has been studied in a variety of experi-
mental investigations using fixed beds (1, 2, 8-12, 17), fluidized beds (3, 4, 12,
17), and dilute solid-phase systems (5-7, 13-16, 19, 20). In spite of the extensive
amount of information obtained from these studies, however, primary emphasis in
the development of kinetic correlations has been placed on description of the total
methane yields obtained after relative deactivation of coal solids has occurred
rather than on the more detailed behavior occurring during the transient period of
"rapid-rate" methane formation.

An experimental study was therefore initiated at the Institute of Gas Technology
(IGT) to supplement existing information, with the objective of quantitatively
characterizing intermediate reaction processes occurring prior to completion of
the rapid-rate methane-formation reaction. This paper discusses some of the
main results obtained thus far in our study of the gasification kinetics of low-rank
coals in hydrogen, helium, and hydrogen-helium mixtures. The kinetic models
developed to describe light gaseous hydrocarbon formation during initial reaction
stages of the coals tested are also described and applied to selected results ob-
tained in other studies directed toward gasification of high-volatile bituminous
coals.

EXPERIMENTAL

A schematic diagram of the experimental apparatus used in the study is shown
in Figure 1; the details of this system have been described previously (13). The
main component of the system is a 1.6-mm internal diameter, 60-m long, helical
coiled transport reactor. The reactor tube itself serves as the heating element
with electrodes attached along the length of the coil to provide nine independent

heating zones. This unique feature permits the establishment of temperature profiles along the length of the reactor tube that correspond to the desired constant heat-up rates of gas-solids mixtures passing through the tube. The reactor can also be operated isothermally. Coal particles (0.074 to 0.089-mm diameter) are mixed with feed gases at the top of the reactor coil, and the dilute gas-solids mixture (less than 0.1% solids by volume) passes through the reactor coil at temperatures very close to those imposed on the reactor wall. The char produced is collected in a sintered metal filter heated to 300°C for subsequent solids analyses. The gas then passes through a condenser system to collect water and condensable hydrocarbons. The dry gas is analyzed with a mass spectrograph (periodic samples) for major gaseous species and, in some tests, with a flame ionization detector for the concentration of total carbon in hydrocarbon species.

Steady-state conditions are achieved in less than 1 minute after initiation of gas and coal flows, and sufficiently large gas/solid feed ratios are employed to result in less than 5% dilution of the dry exit gas with reaction products. Thus, the partial pressures of feed-gas components remain essentially constant throughout the reactor tube. The main gaseous products measured include carbon monoxide (CO), carbon dioxide (CO_2), hydrogen (H_2), methane (CH_4), and ethane (C_2H_6). Other noncondensable gaseous hydrocarbons, particularly three- and four-carbon aliphatics and possibly some ethylene, were not usually accurately measured with the mass spectrograph due to the low concentrations present. The total carbon in this species group, referred to as C_3+, was determined by difference — that is, by subtracting the carbon in methane and ethane from the total carbon in gaseous hydrocarbon species determined by flame ionization detection. Condensable liquid products were also difficult to quantitatively recover in the laboratory-scale equipment due to the relatively small quantities available. Product water was therefore determined by an oxygen balance and condensable oils and tars by a carbon balance.

TYPICAL RESULTS

The gasification kinetics of three low-rank coals — Montana lignite, Montana subbituminous coal, and North Dakota lignite — were investigated. The compositions of these three coals are given in Table 1, which also includes compositions of several other coals referred to in this paper.

Figure 2 shows some typical product yields obtained for gasification of Montana lignite in hydrogen at 35 atm under conditions of a constant heat-up rate of 30°C/s. With this lignite, devolatilization initiates at some temperature below 500°C. Coal oxygen is evolved primarily as carbon dioxide, carbon monoxide, and water, with a small amount being observed in phenolic oils. Carbon dioxide evolution occurs below 500°C, apparently resulting from decomposition of carboxyl functional groups. Decomposition of other oxygenated functional groups leads to evolution of both carbon dioxide and water, with total available coal oxygen evolution being completed at about 700°C. This is shown more clearly in Figure 3. Although carbon dioxide yields begin decreasing above 650°C, this is due solely to the secondary reaction —

$$CO_2 + H_2 \rightarrow CO + H_2O$$
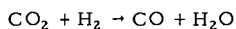
occurring in the reactor coil, probably catalyzed by the reactor walls.

18

Table 1. COAL ANALYSES

| | Montana Lignite | Montana Subbituminous (This Study) | North Dakota Lignite | Pennsylvania High-Volatile A Bituminous | | | Illinois High-Volatile C Bituminous (Ref. 6) | Illinois High-Volatile Bituminous (Ref. 9) | Warwickshire (Eng.) High-Volatile Bituminous (Ref. 16) |
				(Ref. 6)	(Ref. 14)	(Ref. 11)			
Ultimate Analysis, wt% (MAF)									
Carbon	68.61	73.10	70.30	83.93	84.00	82.81	80.26	77.59	80.70
Hydrogen	4.35	4.53	4.47	5.54	5.70	5.69	5.44	5.80	5.86
Oxygen	25.50	19.73	23.60	7.66	7.10	7.70	11.07	10.58	13.44
Nitrogen	0.94	1.16	0.99	1.70	1.70	1.68	1.83	1.25	13.44
Sulfur	0.60	1.48	0.64	1.17	1.50	2.12	1.40	4.78	13.44
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Proximate Analysis, wt% (MAF)									
Volatile Matter	45.95	42.45	44.91	39.10	40.90	37.83	39.69	--	38.94
Fixed Carbon	54.05	57.55	55.09	60.90	59.10	62.17	60.31	--	61.06
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	--	100.00

19

Oil and tar as well as C_3+ gaseous hydrocarbon evolution occurs below 550°C. C_3+ gaseous hydrocarbon yields decrease, however, above 650°C due to hydrogenation to methane and ethane. Total yields of oil and tar remain relatively constant up to 850°C, although the composition of this fraction changes substantially with increasing temperature, becoming lighter in nature. Conversion of heavier oils to benzene initiates at about 650°C, and, at 850°C, approximately one-half of the total oil/tar fraction consists of benzene.

Methane-plus-ethane yields[*] increase continuously with increasing temperature, with rates of formation becoming substantial above 600°C. Above 700°C, when primary devolatilization processes are virtually completed, gasification of the intermediate coal structure (semi-char) is the primary reaction that occurs concurrently with the secondary devolatilization of coal hydrogen, leading to the formation of relatively nonreactive coal char. Methane-plus-ethane yields increase significantly with increasing hydrogen pressure, as shown in Figure 4. This contrasts with the kinetics of evolution of primary devolatilization products, which depend for the most part on time-temperature history and not on gas composition or pressure over the ranges of these variables employed.

The main qualitative features exhibited for gasification of Montana lignite in hydrogen at a heat-up rate of 30°C/s were also observed for the other coals tested and for other time-temperature histories. As would be expected, yield-versus-temperature curves such as those shown in Figure 2 are shifted somewhat toward higher temperatures at an increased heating rate of 80°C/s and are shifted toward lower temperatures for isothermal operation with a gas-solids residence time of 7 seconds. Significantly, however, the maximum yields of primary devolatilization products (carbon dioxide, carbon monoxide, water, oils and tars, and C_3+ gaseous hydrocarbons) that can be achieved at sufficiently high temperatures appear to depend solely on coal type rather than on pressure, gas composition, or time-temperature history. This behavior is probably typical only of noncaking low-rank coals. With caking bituminous coals different behavior would be expected, particularly with respect to maximum oil and tar yields, which tend to increase with increased heat-up rate, decreased coal-particle size, and decreased total pressure.

DATA ANALYSIS

A primary objective of this investigation is to quantitatively describe the kinetics of the initial-stage methane-plus-ethane formation for different coals as a function of hydrogen partial pressure and coal time-temperature history. The total methane-plus-ethane yields obtained in the gasification of coals with hydrogen result primarily from three overall reaction processes: direct coal hydrogenation, thermally activated coal-decomposition reactions, and secondary hydrogenation of C_3+ gaseous hydrocarbons. Although some methane and ethane could also be formed by hydrogenation of light oils such as benzene, these reactions should not occur significantly at the conditions employed in this study (18).

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[*] Methane and ethane yields are grouped together since it has been previously shown (13) to be likely that, after initial devolatilization, both species are direct products of hydrogen gasification of the coal.

Methane and Ethane From Coal-Decomposition and Secondary Hydrogenation Reactions

In order to isolate the kinetics of direct coal hydrogenation, it is necessary to determine the contributions of coal-decomposition reactions and secondary hydrogenation reactions to total methane-plus-ethane yields. Since a fundamental approach to such evaluations would be extraordinarily complex, if practically possible at all, simplifying approximations and assumptions were made to obtain first-order estimates. Figure 5 shows methane-plus-ethane yields obtained for gasification of Montana lignite in helium at 35 atm for a constant heat-up rate of 30°C/s, and for isothermal operation with a coal-gas residence time of 7 seconds. Based on these data, the methane-plus-ethane obtained from coal decomposition was assumed to occur in two stages: below 600°C a fixed fraction is instantaneously evolved, and, above this temperature, yields increase linearly with increasing temperature up to 780°C when conversion is complete. The assumption that the kinetics of this reaction are independent of coal residence time implies a wide distribution of activation energies for the decomposition steps leading to methane-plus-ethane formation. It was also assumed that the kinetics of this decomposition reaction in a helium atmosphere also apply in a hydrogen atmosphere.

Figure 6 shows yields of C_3+ gaseous hydrocarbons obtained in hydrogen and in helium for gasification of Montana lignite at a coal heat-up rate of 30°C/s. In helium the C_3+ hydrocarbons initially formed do not undergo pyrolysis at higher temperatures up to 810°C, whereas, in hydrogen the yield of this fraction begins to decrease above about 600°C due to hydrogenation to methane and ethane. The overall hydrogenation reactions occurring were assumed to be equivalent to a single first-order reaction:

$$C_3+ \text{ gaseous hydrocarbons} \xrightarrow{ k_4 } \text{methane-plus-ethane}$$
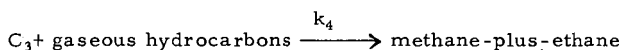
The complete correlation to describe methane-plus-ethane formation from coal thermal decomposition and hydrogenation of C_3+ hydrocarbons has the following form:

$$N = N_0 \left[\alpha' X' + \alpha'' X'' + \alpha''' X''' \right] \qquad\qquad 1)$$

where,

X' = conversion fraction of thermal decomposition reactions below 600°C

X'' = conversion fraction of thermal decomposition reactions above 600°C

X''' = conversion fraction of C_3+ hydrogenation reactions

N_0 = total carbon in methane-plus-ethane that can be formed from thermal decomposition and C_3+ hydrogenation reactions, g-atom/g-atom feed carbon in coal

N = carbon in methane-plus-ethane formed from thermal decomposition and C_3+ hydrogenation reactions at any time, g-atom/g-atom feed carbon in coal

$\alpha', \alpha'', \alpha'''$ = coefficients defining the distribution of carbon that can be converted to methane-plus-ethane from the three reactant groups considered.

Based on data obtained with the three low-rank coals used in this study, and on some limited data available in the literature for gasification of a bituminous coal in hydrogen, the following numerical evaluations were made:

$$\alpha' = 0.2$$
$$\alpha'' = 0.3$$
$$\alpha''' = 0.5$$

	N_0, g-atom carbon/g-atom feed carbon in coal
lignite	0.05
subbituminous coal	0.08
bituminous coal	0.10

$$X' = 1.0$$

$$X'' = 0 \text{ at } T < 873°K$$

$$X'' = 0.00555T - 4.845 \text{ for } 873° \leq T \leq 1053°K \qquad \qquad 2)$$

$$X'' = 1.0 \text{ for } T > 1053°K$$

and,

$$\frac{dX'''}{d\theta} = k_4(1 - X''')$$

$$k_4 = 1.7(10^4)\exp(-11,830/T), \text{ s}^{-1} \qquad \qquad 3)$$

where,

T = temperature; °K in Equations 2 and 3

θ = time, s.

Although the model described above is much oversimplified, it does provide an approximate basis consistent with the data obtained to numerically adjust methane-plus-ethane yields to correspond only to direct coal hydrogenation.

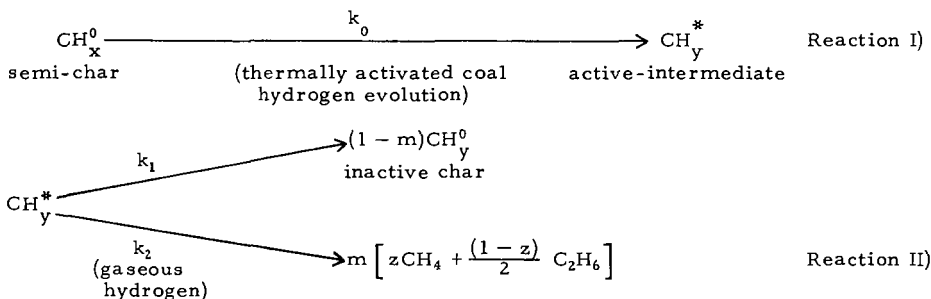Kinetics of Direct Coal Hydrogenation

In a previous paper (13), a model was proposed to describe the kinetics of the initial stages of direct coal hydrogenation, based only on data obtained with Montana lignite and using a different method to adjust methane-plus-ethane yields than is described above. These data were reevaluated in the context of all the data available at the present time, using the same model assumed previously but with modified and more generally applicable evaluations of kinetic parameters.

A main feature leading to the development of the model is the strong correlation that exists between adjusted methane-plus-ethane yields and coal hydrogen evolution during the secondary devolatilization stage. This behavior is shown in Figure 7 where, at constant hydrogen partial pressure, methane-plus-ethane yields are directly proportional to the secondary coal hydrogen evolved, independent of time-temperature history. Conveniently, the trends exhibited at a specific pressure level cannot be differentiated for the different coals considered. The slopes of the lines drawn in Figure 7 increase with increasing hydrogen pressure, consistent

with qualitative observations made in other investigations of the rapid-rate methane phenomenon.

Variations in coal hydrogen evolution with increasing temperature are described in Figure 8. For a given time-temperature history the amount of coal hydrogen evolved is essentially independent of gaseous hydrogen pressure, and the results obtained with Montana lignite (Figure 8A) show similar behavior in both helium and hydrogen atmospheres.

The results given in Figures 7 and 8 suggest that the formation of active sites, which promote methane-plus-ethane formation through interaction of gaseous hydrogen with the coal, is directly related to the processes in which coal hydrogen is evolved; this latter process involves only thermally activated phenomena occurring independently of gaseous atmosphere and dependent only on time-temperature history. A formal representation of this model is given by the following reactions:

$$CH_x^0 \xrightarrow{\quad k_0 \quad} CH_y^* \qquad \text{Reaction I)}$$

semi-char   (thermally activated coal   active-intermediate
hydrogen evolution)

$$CH_y^* \begin{cases} \xrightarrow{k_1} (1-m)CH_y^0 \quad \text{inactive char} \\ \\ \xrightarrow[\substack{(gaseous \\ hydrogen)}]{k_2} m\left[zCH_4 + \dfrac{(1-z)}{2}\, C_2H_6 \right] \end{cases} \qquad \text{Reaction II)}$$

where,

x = atomic ratio of hydrogen to carbon in CH_x^0

y = atomic ratio of hydrogen to carbon in CH_y^* and CH_y^0

z = fraction of carbon gasified as methane in Reaction II

k_0, k_1, k_2 = first-order rate constants, s^{-1}

m = $k_2/(k_1 + k_2)$.

For purposes of quantitative correlation the following definitions are made:

Y = total carbon in adjusted methane-plus-ethane yields, g-atom/g-atom feed carbon

n_H = total coal hydrogen gasified at any time, g-atom/g-atom feed carbon

n_H^0 = total coal hydrogen gasified during primary devolatilization, g-atom/g-atom feed carbon

λ = fraction of total feed carbon not evolved as primary devolatilization products (closely related to fixed carbon), g-atom/g-atom feed carbon.

With this model the rate of Reaction I is assumed to be limiting, with the rate of Reaction II being very fast. In addition the ratio k_2/k_1 is assumed to be temperature-independent. From these definitions the conversion fraction, f, of the semi-char CH_x^0 to active-intermediate CH_y^* can be expressed by the relationship:

$$f = Y/m\lambda = (n_H - n_H^0)/(x - y + my)\lambda \qquad 4)$$

From Equation 4 the methane-plus-ethane yield, Y, is related to coal hydrogen evolved by:

$$Y = \frac{m(n_H - n_H^0)}{(x - y + my)} \qquad 5)$$

or,

$$Y = S(n_H - n_H^0) \qquad 6)$$

where,

$$S = \frac{m}{(x - y + my)} \qquad 7)$$

Equation 6 is consistent with the trends given in Figure 7. The slopes, S, of the lines drawn in Figure 7 are tabulated in Table 2, and the value of n_H^0 estimated from Figure 7 is about 0.27, corresponding to the value of coal hydrogen evolved due to primary devolatilization reactions.

The following independent relationship also results from the model assumed:

$$Y(1/S - Z) = \lambda(x - Z) \qquad 8)$$

where,

Z = the atomic hydrogen-to-carbon ratio in the coal at any time during gasification

Table 2. VARIATION IN S WITH HYDROGEN PRESSURE

Hydrogen Pressure, atm	S, g-atom carbon/g-atom hydrogen
18	0.24
35	0.41
52	0.56

Using values of S given in Table 2, at appropriate hydrogen pressures, values of the term $Y(1/S - Z)$ were plotted versus Z for the three coals tested and for the bituminous coal study to yield values of λ and x. A value of $\lambda = 0.80$ was applicable for all the coals considered. A value of $x = 0.65$, obtained for the bituminous coal, was slightly higher than a value of $x = 0.62$, obtained for the two lignites and the subbituminous coal. With these evaluations, values of m were computed as a function of pressure by rearranging Equation 7:

$$m = \frac{S(x - y)}{1 - Sy} \qquad 9)$$

with a value of $y = 0.10$ assumed as a nominal average value based on gasification data obtained with different coals at elevated temperatures for extended times.

Values of m and corresponding values of k_2/k_1 are given in Table 3, and values of k_2/k_1 are plotted versus hydrogen pressure in Figure 9. The linear relationship shown in Figure 9 is represented by the equation:

$$k_2/k_1 = 0.0083P_H \qquad \text{10)}$$

where,

P_H = hydrogen partial pressure, atm.

Table 3. VARIATION OF m AND k_2/k_1 WITH HYDROGEN PRESSURE

Hydrogen Pressure, atm	m	k_2/k_1
18	0.127	0.145
35	0.225	0.290
52	0.307	0.443

From the evaluations made, the adjusted methane-plus-ethane yield is related to the conversion fraction, f, of the semi-char by the relationship:

$$Y = m\lambda f = \frac{0.00664P_H}{1 + 0.0083P_H} \cdot f \qquad \text{11)}$$

In analyzing the kinetics of Reaction I to quantitatively define the functional dependence of f on reaction conditions, the same model described in a previous paper was adopted. The main assumptions of this model are as follows:

- CH_x^0 reacts according to Reaction I by a first-order process, but where there is a distribution of activation energies for the first-order rate constant, k_0.

- The distribution function of activation energies is a constant; i.e., $f(E)dE$ = fraction of total carbon in which the activation energy, E, in the rate constant —

$$k_0 = k_0^0 \exp(-E/RT)$$

is between E and (E + dE).

where,

$f(E)$ = 0 for $E < E_0$

$f(E)$ = C (constant) for $E_0 \le E \le E_1$

$f(E)$ = 0 for $E > E_1$

k_0^0 = pre-exponential factor, s^{-1}

Note that because —

$$\int_{E_0}^{E_1} CdE = 1$$

then —

$$C = 1/(E_1 - E_0)$$

From these assumptions, the average conversion fraction of CH_x^0 can be expressed by the following relationship for any time-temperature history:

$$1 - f = \frac{1}{E_1 - E_0} \int_{E_0}^{E_1} \left\{ \exp \left[-k_0^0 \int_0^\theta \exp(-E/RT) d\theta \right] \right\} dE \qquad 12)$$

Statistical procedures were used to evaluate the parameters k_0^0, E_0, and E_1 given below, based on best consistency of experimental values of f computed from Equation 4 and calculated values of f computed from Equation 12 for the appropriate time-temperature history:

k_0^0 = $1.97(10^{-10})$, s^{-1}

E_0 = 40.8 kcal/g-mol

E_1 = 62.9 kcal/g-mol.

A comparison between experimental and calculated values of f is given in Figure 10. A comparison of experimental total methane-plus-ethane yields and values calculated from the models and numerical evaluations presented in this paper is given in Figure 11.

Although it may be tempting to consider theoretical implications concerning the detailed mechanisms of coal hydrogen evolution during secondary devolatilization, based on the values of k_0, E_0, and E_1 given above, such considerations should be made cautiously. Because of the sensitivity of these evaluations to the statistical numerical procedures employed, and because of the strong covariance between these parameters, significantly different evaluations can be made to reasonably describe data obtained over a wide range of conditions. This point is illustrated in Figure 12, where variations in values of conversion, f, that were calculated using values of the kinetic parameters determined in this study are compared to values of f calculated using a significantly different set that nevertheless describes the same data quite well. This is particularly true for coal residence times ranging from 1 to 10 seconds, which represent the range of conditions most commonly employed in various investigations of initial coal gasification kinetics. The illustration in Figure 12 was constructed to show the magnitude of differences in evaluation of kinetic parameters that could occur in describing data obtained over a wide range of residence times and temperatures for isothermal conditions. Much greater ranges of estimates could result, however, in describing conversions obtained at a single residence time over a wide range of temperatures, or, alternatively, at a single temperature over a wide range of residence times. Thus, although the model proposed does suggest a mechanistic relationship between coal hydrogen evolution and active site formation for coal hydrogenation, the numerical evaluations made to facilitate practical application of the information obtained for reactor design do not provide a substantial basis for a more detailed mechanistic understanding.

Application of Model to Bituminous Coal Gasification

The experimental study described has been limited to use of low-rank coals to minimize plugging of the small-diameter reactor tube employed. It was of interest, however, to make an approximate analysis of some data obtained in other investigations concerned with gasification of high-volatile bituminous coals in

hydrogen-containing gases to obtain an indication of the possible applicability of
the model developed to describe behavior with bituminous coals. Figure 13 shows
yields of methane-plus-ethane obtained in a variety of studies conducted over a
wide range of conditions. Indicated values of coal and gas residence times and
hydrogen partial pressures were either reported directly or were deduced from
other reported information. The hydrogen partial pressure used for correlation
corresponds to the product gas. For systems where significant conversion of
the feed gas occurs, which is the case in most of the systems considered, this
representation assumes substantial backmixing in the gasification reactor. In
all of the studies, either hydrogen or hydrogen-methane mixtures were used as
feed gases. The analyses of the feed coals used in the various studies are
included in Table 1.

In interpreting the data given in Figure 13, the model developed in this study
was assumed. According to this model, experimental values of the function m
should vary with hydrogen pressure according to the expression:

$$m = \frac{0.0083P_H}{1 + 0.0083P_H}$$ 13)

Values of m were computed from experimental values of adjusted methane-plus-
ethane yield, Y, using the expression:

$$m = Y/\lambda f$$

where $\lambda = 0.80$. Values of Y were computed by subtracting the values of N computed
from Equation 1 from the experimental values of total methane-plus-ethane yield.
Evaluations of N were made for the appropriate reported gas-solids residence
times and reaction temperatures, using a value of $N_0 = 0.10$, estimated for
bituminous coal. Values of f were computed using Equation 9 (with values of
k_0^0, E_0, and E_1 developed in this study), also at the reported reaction conditions.

In Figure 14, the values of m computed from experimental results obtained with
bituminous coals are compared to Equation 13. For hydrogen partial pressures up
to about 120 atm, reasonable consistency exists, suggesting that the model de-
veloped is applicable for gasification of bituminous coals as well as for gasification
of subbituminous coals and lignites.

SUMMARY

The results obtained in this study indicate that the initial gasification of low-rank
coals in hydrogen-containing gases at elevated pressures occurs in two stages.
The first stage involves thermally activated devolatilization reactions resulting
in the evolution of carbon oxides, water, oil and tar, and some light gaseous
hydrocarbons, and leading to the formation of an intermediate semi-char. The
second stage occurs consecutive to primary devolatilization and involves
thermally activated decomposition reactions associated with the secondary de-
volatilization of remaining coal hydrogen, leading to the formation of a relatively
nonreactive char. Significantly, yields of methane-plus-ethane, other than that
derived from thermal coal-decomposition reactions or from C_3+ light hydrocarbon
hydrogenation reactions, are stoichiometrically related to coal hydrogen evolved
during the secondary devolatilization stage. This has suggested a model in which
the transitions that occur in conversion of semi-char to char, with associated
coal hydrogen evolution, involve the formation of a reactive intermediate carbon

27

structure that can either rapidly react with gaseous hydrogen to form methane and ethane or can convert to nonreactive char. The ratio of methane-plus-ethane formation to char formation is independent of temperature but is directly proportional to hydrogen partial pressure.

A numerical representation of this model permits detailed prediction of the kinetics of methane-plus-ethane formation for practical application to reactor design for systems using low-rank coals. A strong possibility that this model might also be suitable for application to gasification of high-volatile bituminous coal was also suggested, based on analyses of some available data obtained in other investigations.

ACKNOWLEDGMENT

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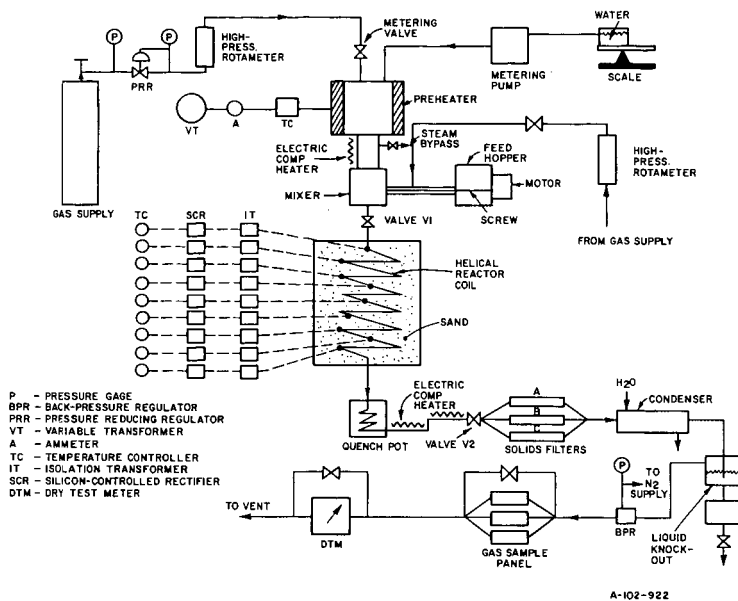
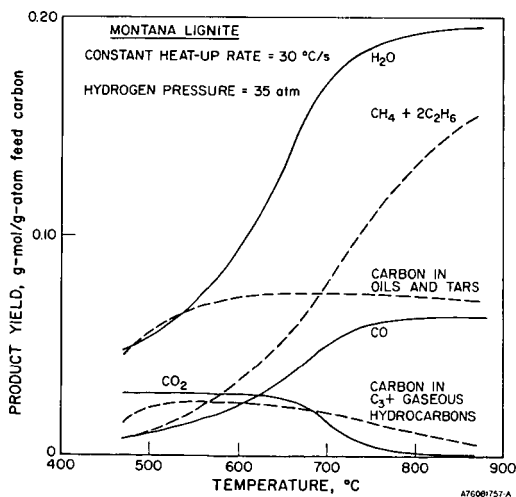Figure 1.   DIAGRAM OF THE EXPERIMENTAL SYSTEM

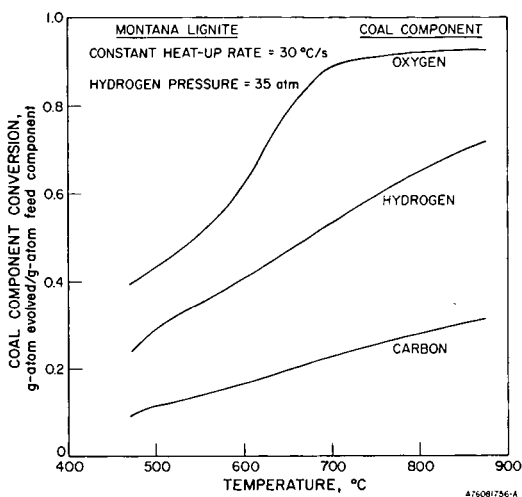Figure 2.   TYPICAL PRODUCT YIELDS FOR GASIFICATION IN HYDROGEN

30

Figure 3. TYPICAL COAL COMPONENT CONVERSION
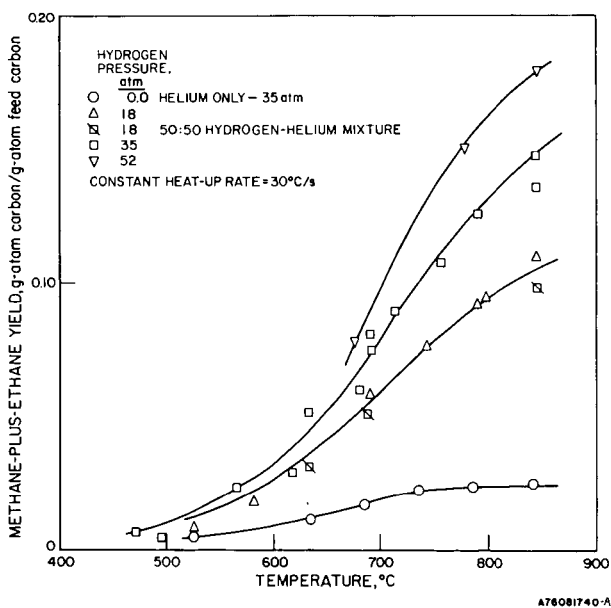DURING GASIFICATION IN HYDROGEN

Figure 4. EFFECT OF PRESSURE ON TOTAL METHANE-PLUS-ETHANE
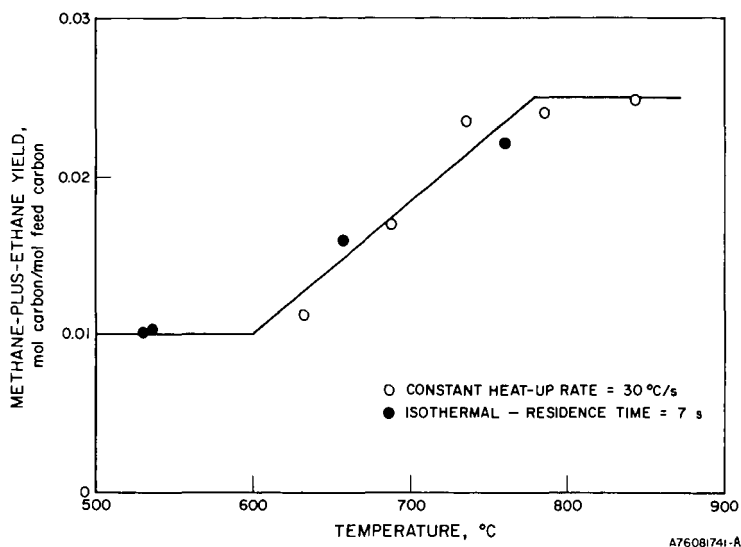YIELDS DURING GASIFICATION OF MONTANA LIGNITE

31

Figure 5.   METHANE-PLUS-ETHANE YIELDS FROM PYROLYSIS OF
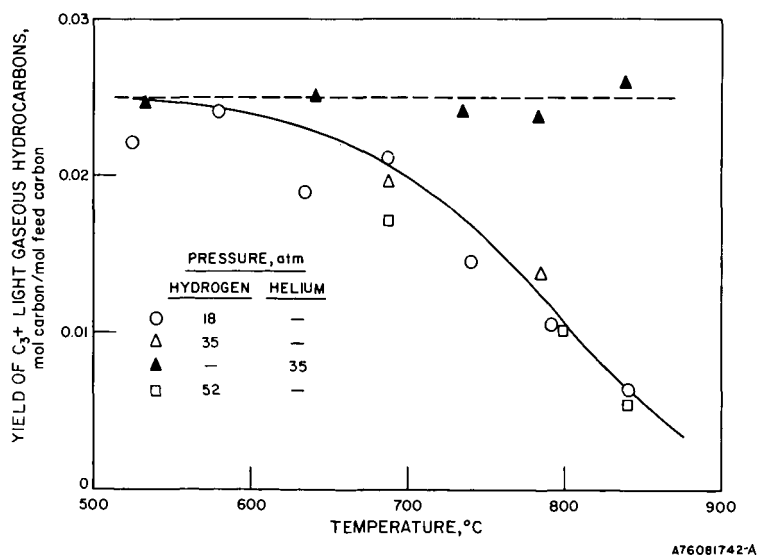MONTANA LIGNITE IN HELIUM AT 35 atm

Figure 6. C_3+ LIGHT GASEOUS HYDROCARBON YIELDS FROM
GASIFICATION OF MONTANA LIGNITE IN HYDROGEN OR HELIUM
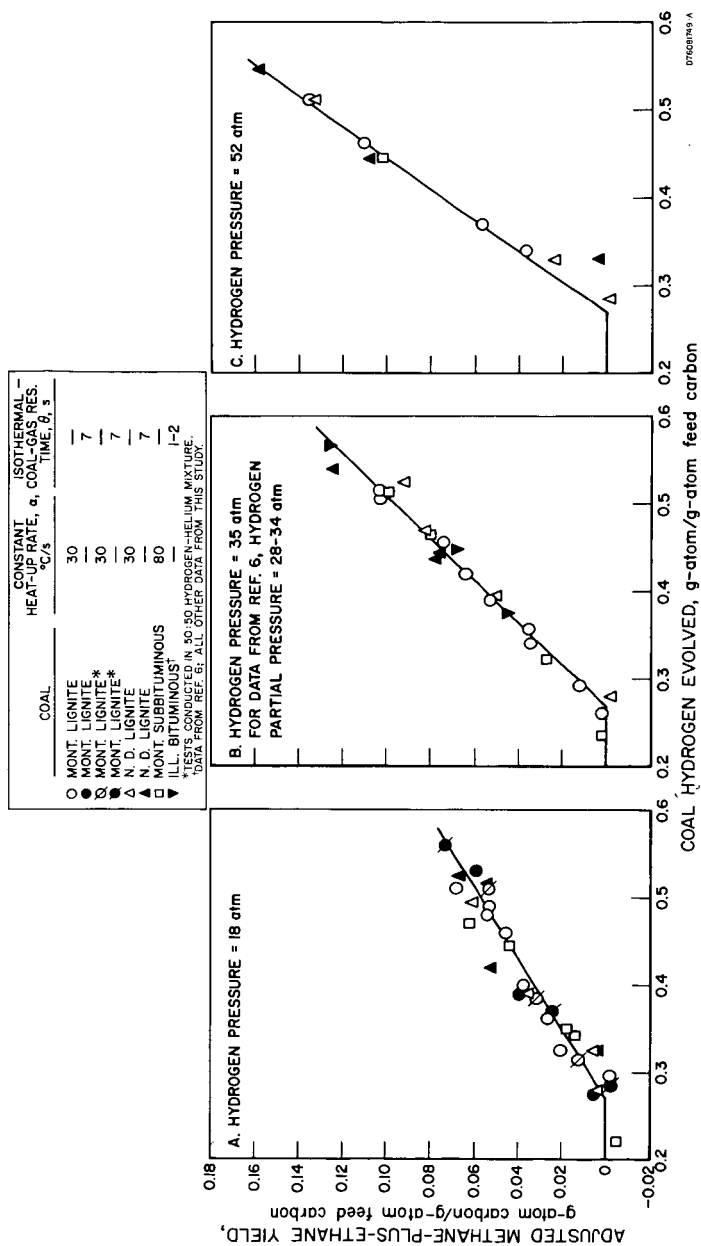(Constant Gas-Coal Heat-Up Rate = 30^0C/s)

Figure 7. STOICHIOMETRIC RELATIONSHIP BETWEEN
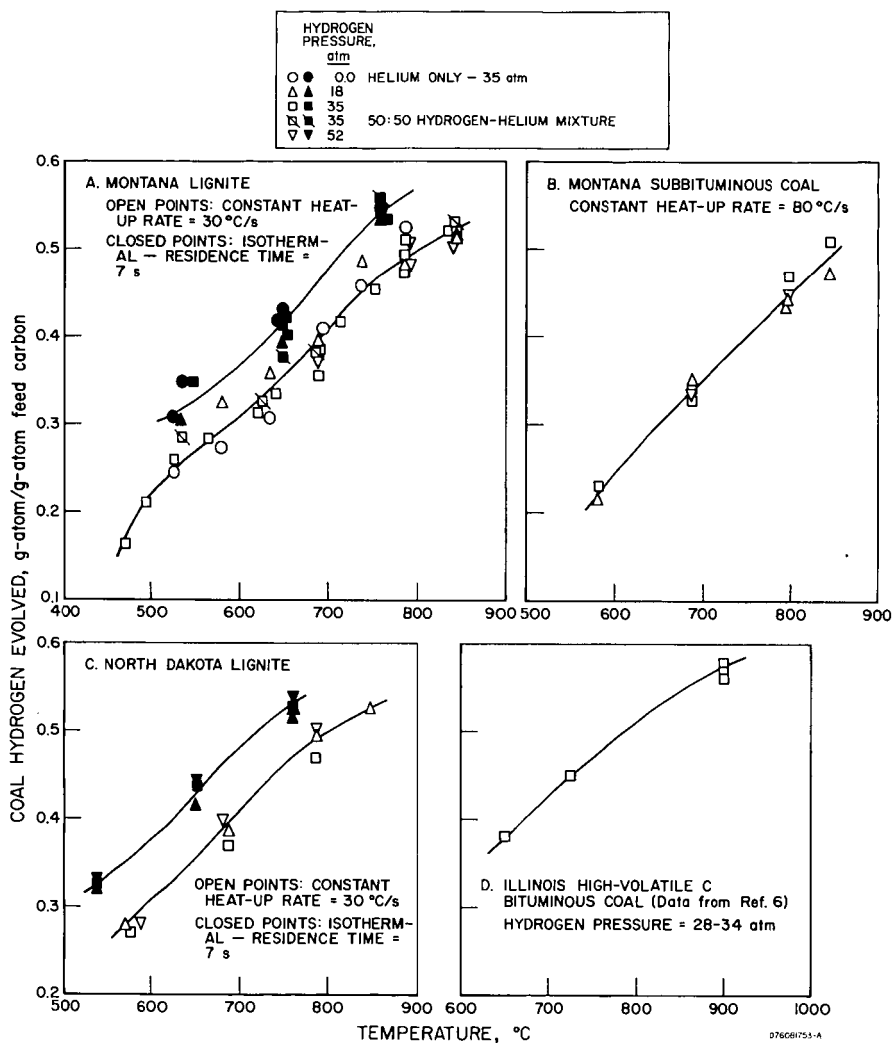ADJUSTED METHANE-PLUS-ETHANE YIELD AND COAL HYDROGEN EVOLUTION

33

Figure 8. COAL HYDROGEN EVOLUTION DURING GASIFICATION
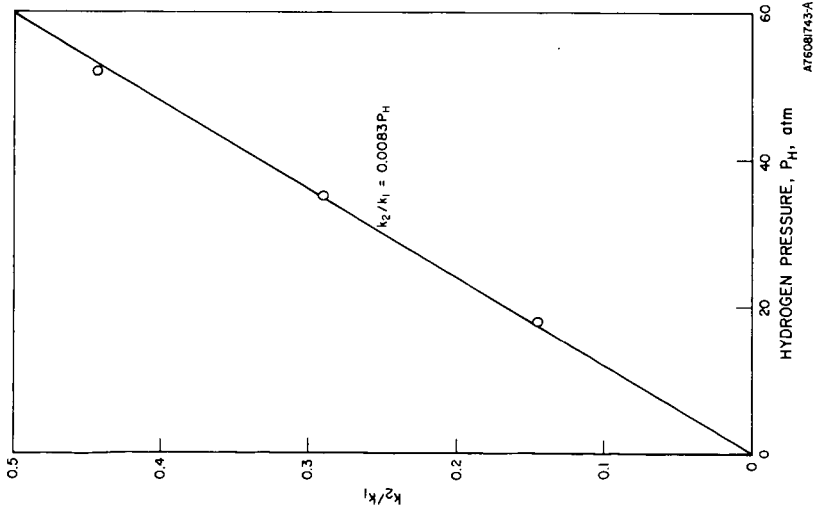OF DIFFERENT COALS

34

Figure 10. COMPARISON OF CALCULATED AND
EXPERIMENTAL COAL HYDROGEN CONVERSION

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COAL HYDROGEN CONVERSION PARAMETER, f

TEMPERATURE, °C

COAL	HYDROGEN PRESSURE, atm	CONSTANT HEAT-UP RATE, a, °C/s	ISOTHERMAL—COAL/GAS RESIDENCE TIME, θ, s
○ MONT. LIGNITE	18-52	30	—
● MONT. LIGNITE	18-35	—	7
△ N.D. LIGNITE	18-52	30	—
▲ N.D. LIGNITE	18-52	—	7
□ MONT. SUBBITUMINOUS	18-52	80	—
▼ ILL. BITUMINOUS (Ref.6)	28-34	—	1-2

CALCULATED { —— CONSTANT HEAT-UP RATE
             - - - ISOTHERMAL

$a = 30°C/s$
$a = 80°C/s$
$\theta = 7$ s
$\theta = 2$ s
$\theta = 1$ s

Figure 9. CORRELATION OF RELATIVE RATE
RATIO, k_2/k_1, WITH HYDROGEN PRESSURE

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HYDROGEN PRESSURE, P_H, atm

k_2/k_1

$k_2/k_1 = 0.0083 P_H$

Figure 12. COMPARISON OF MODEL CHARACTERISTICS
WITH DIFFERENT SETS OF KINETIC PARAMETERS

$$1 - f = \frac{1}{E_1 - E_0} \int_{E_0}^{E_1} e^{-k_0 \theta e^{-E/RT}} dE$$

TIME, θ, s

CONVERSION FRACTION, f

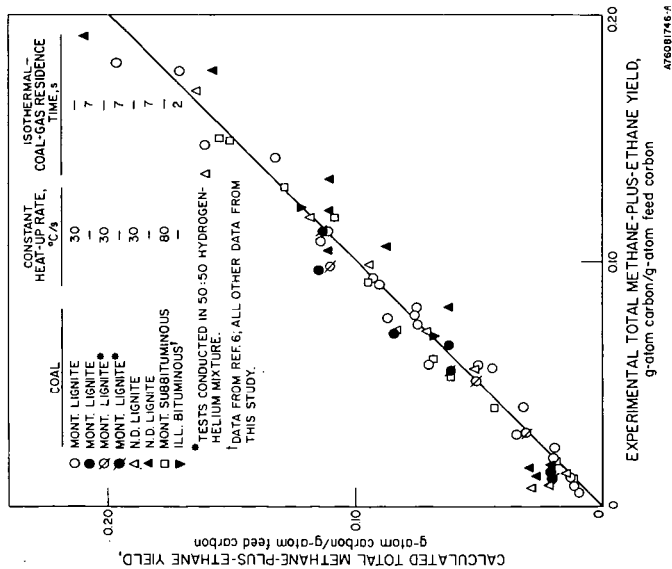| k_0, s^{-1}	E_0	E_1
	—kcal/g-mol—	
$1.97 \cdot 10^{10}$	40.8	62.9
1.86×10^{13}	51.84	79.43

TEMPERATURE, °C

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Figure 11. COMPARISON OF CALCULATED
AND EXPERIMENTAL TOTAL
METHANE-PLUS-ETHANE YIELDS

CALCULATED TOTAL METHANE-PLUS-ETHANE YIELD,
g-atom carbon/g-atom feed carbon

EXPERIMENTAL TOTAL METHANE-PLUS-ETHANE YIELD,
g-atom carbon/g-atom feed carbon

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COAL	CONSTANT HEAT-UP RATE, °C/s	ISOTHERMAL COAL-GAS RESIDENCE TIME, s
MONT. LIGNITE	30	1
MONT. LIGNITE	—	7
MONT. LIGNITE	30	1
MONT. LIGNITE	—	1
N.D. LIGNITE	30	7
N.D. LIGNITE	—	1
MONT. SUBBITUMINOUS	80	2
ILL. BITUMINOUS	—	—

TESTS CONDUCTED IN 50:50 HYDROGEN-HELIUM MIXTURE.

DATA FROM REF. 6; ALL OTHER DATA FROM THIS STUDY.

Figure 14. CORRELATION OF METHANE-PLUS-ETHANE YIELDS OBTAINED IN VARIOUS INVESTIGATIONS FOR HIGH-VOLATILE BITUMINOUS COAL GASIFICATION IN HYDROGEN
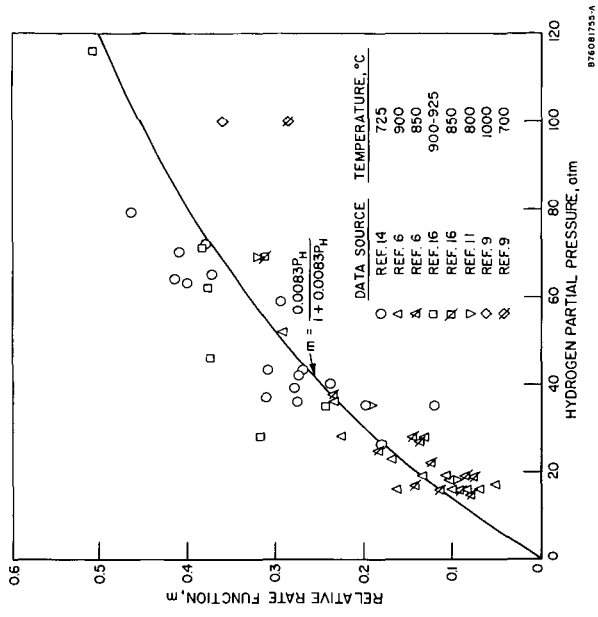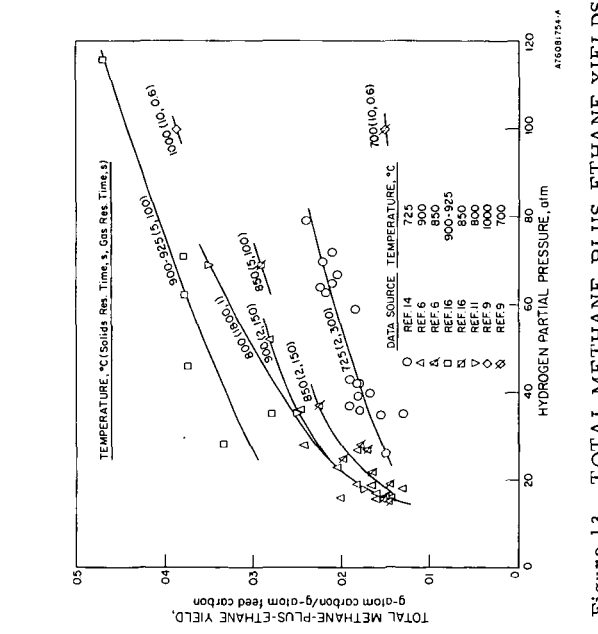

Figure 13. TOTAL METHANE-PLUS-ETHANE YIELDS OBTAINED IN DIFFERENT STUDIES FOR GASIFICATION OF BITUMINOUS COALS WITH HYDROGEN